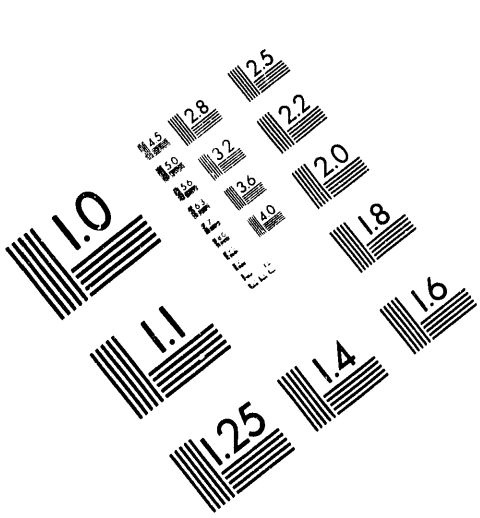

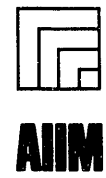

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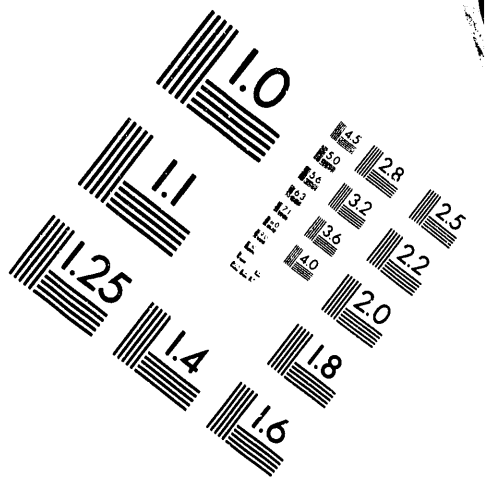

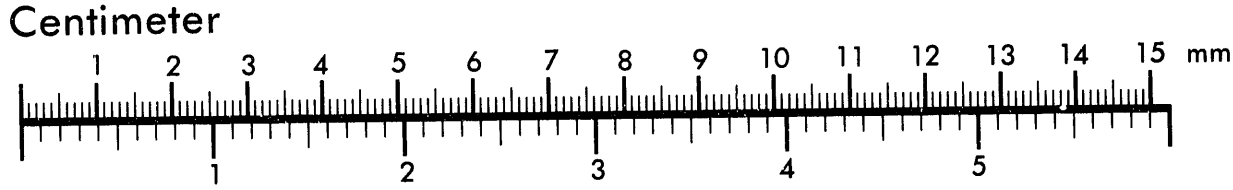

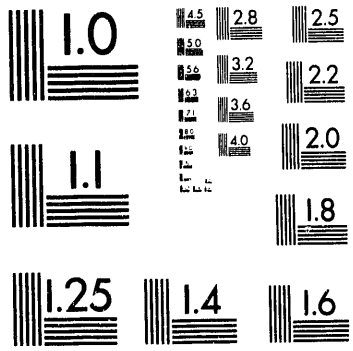

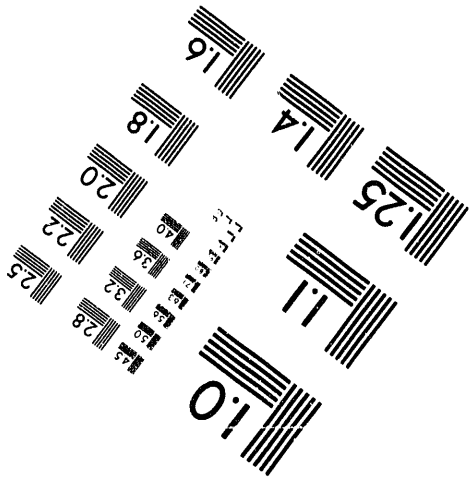

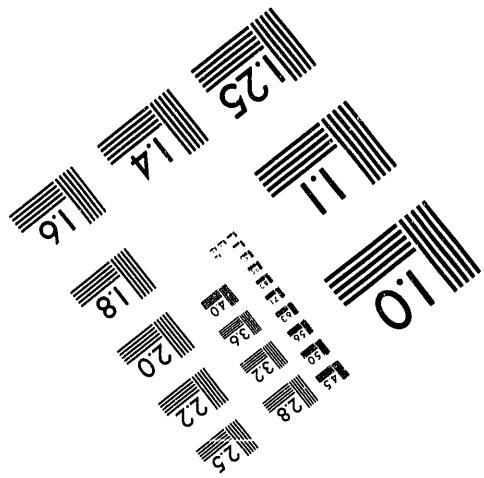

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NOBLE METAL BEHAVIOR DURING MELTING OF SIMULATED HIGH-LEVEL NUCLEAR WASTE GLASS FEEDS

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NOBLE METAL BEHAVIOR DURING MELTING OF SIMULATED HIGH-LEVEL NUCLEAR WASTE GLASS FEEDS

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Noble metals and their oxides can settle in waste glass melters and cause electrical shorting. Simulated waste feeds from Hanford, Savannah River, and Germany were heat treated for 1 hour in a gradient furnace at temperatures ranging from approximately 600°C - 1000°C and examined by electron microscopy to determine shapes, sizes, and distribution of noble metal particles as a function of temperature. Individual noble metal particles and agglomerates of rhodium (Rh), ruthenium (RuO_2), and palladium (Pd), as well as their alloys, were seen. The majority of particles and agglomerates were generally less than 10 microns; however, large agglomerations (up to 1 mm) were found in the German feed. Detailed particle distribution and characterization was performed for a Hanford waste to provide input to computer modeling of particle settling in the melter.

INTRODUCTION

The reprocessing of nuclear fuel generates a form of high-level radioactive waste that will be treated further to produce a low-solubility, low-mobility glass suitable for geologic or long-term disposal. In many countries, including the United States, current plans call for vitrification of the high-level and transuranic fraction of these wastes to form a borosilicate glass that is resistant to radioactive damage and leaching. At Hanford, wastes have been generated over the span of 45 years from fuel reprocessing and other operations. These wastes, like other nuclear fuel reprocessing wastes, contain platinum group metals, also known as noble metals. The solubility of noble metals (e.g., palladium, rhodium, and ruthenium) in glass-forming melts is typically extremely low. Undissolved noble metal particles can agglomerate, creating regions of heterogeneous nucleation, which influence the viscosity and uniformity of the glass in the melter. The size and behavior of the noble metal particles in the glass tank will determine whether a significant quantity of the metal will settle to the floor of the melter or be carried out in the glass discharged to the canister. Many of the noble metal oxides and alloys are excellent electrical conductors. If a sufficient quantity of noble metals settles to the melter floor, the lower electrodes could be electrically

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*Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

shorted. If this occurs, then the noble metal accumulation would need to be removed or the melter would have to be replaced. Significant work has been done in characterizing noble metals in glass melts and their settling behavior in melters[1,2,3,4,5].

To determine the impact of the noble metals on the operational life of the reference Hanford Waste Vitrification Plant (HWVP) melter, an integrated testing and modeling approach was begun. The Gradient Furnace Testing (GFT) was the first step of this approach.

The general objective of this work was to determine the behavior of the noble metals in the nominal HWVP melter feed simulant as it progresses through the various reaction layers of the melter cold cap. Specifically, testing provided noble metal particle characteristics, including size, shape, chemical/alloy composition, and extent of agglomeration. These characteristics were used to provide the upper boundary condition for computer modeling of the melter. This modeling is being done in conjunction with melter tests to predict the effect of noble metal settling on the melter life.

A secondary objective was to establish the relative differences between the nominal HWVP melter feed and Kernforschungszentrum Karlsruhe (KfK) and Defense Waste Processing Facility (DWPF) feeds, regarding noble metal particle formation and characteristics.

In order to simulate the cold cap of a melter at laboratory-scale, the gradient furnace was used, in which simulated dried feed was subjected to a linear temperature gradient horizontally along its length. The gradient produced conditions similar to those in a melter cold cap. The laboratory-scale testing was done using simulated melter feeds for the Hanford Waste Vitrification Plant (HWVP), the Defense Waste Processing Facility (DWPF), and Kernforschungszentrum Karlsruhe (KfK) in Germany.

The feeds differed in composition, but were prepared in generally the same way. A slurry was prepared, from hydroxides and nitrates of the waste constituents. For the HWVP and the DWPF feeds, formic acid was then added. Finally, glass frit was added to the slurry. The frit size varied between feeds. For the HWVP and DWPF feeds, the frit size was -80/+200 mesh. For the KfK feed, the frit consisted of glass beads approximately 2 mm in diameter.

Two HWVP feed simulants were used. The difference between the two was the way the noble metals were precipitated in the simulated Neutralized Current Acid Waste (NCAW). In the first feed, the noble metals were precipitated from nitrates along with the major constituents. In the second feed, the noble metals were precipitated from nitrates along with other nitrates that constitute minor constituents. Data for the second HWVP feed (with minors) was used as input to the computer modeling effort.

EXPERIMENTAL PROCEDURE

Each of the four feeds studied was subjected to heat treatment in the gradient furnace and analyzed using optical and scanning electron microscopy (SEM).

The target concentrations of noble metals in the product glasses are shown in Table 1.

Table 1. Concentration of Noble Metals in Glass (Wt%)

Noble Metal	HWVP	DWPF	KfK
RuO_2	0.11	0.1	0.655
Rh	0.024	0.02	0
Pd	0.03	0.03	0.298
SUM	0.097	0.15	0.953

For each sample, the feed was loaded into a 30.5-cm-long boat shaped quartz crucible and held at a specified temperature gradient for 1 hour in the gradient furnace. The furnace produces an adjustable linear temperature gradient of approximately 12°C/cm. For the HWVP-1 and DWPF samples, the range used was 579°C to 928°C. For the HWVP-2 sample the range was 593°C to 936°C, and for the KfK sample it was 698°C to 1046°C. These gradients approximate the gradient found in a melter cold cap. Most cold caps are only 2-10 cm thick. A longer boat was chosen in order to get more distinct temperature zones. The gradient furnace cannot completely simulate the complex behavior of the cold cap[7], but is believed to be sufficient for providing particle characteristics for initial computer modeling.

After removal from the gradient furnace, the samples were annealed for 1 hour at 500°C and cooled slowly overnight. The crucibles were then fixed in an epoxy resin mold and cut in half lengthwise. Six 5-cm segments were made from each sample. Each segment was mounted on a slide, thin-sectioned, and polished for analysis by microscopy.

Each thin section was examined initially with an optical microscope so that general observations could be made regarding gas generation, foaming, and general mixing and melting behavior[7]. Individual noble metal particles were impossible to identify optically. Therefore, SEM was used in the backscatter mode to identify potential noble metal particles. The composition of the particle was then determined by energy dispersive spectrometry (EDS) using a Link Spectrometer at 20 kV. Observations were made of the particle size, shape, composition, and general distribution by temperature range.

RESULTS

Results for the HWVP feed in which noble metals were precipitated with the minor constituents were of primary importance, and are presented here. The input to the computer modeling effort was based on this feed. In addition, comparisons with the other HWVP feed (with majors), the DWPF feed, and the KfK feed are made.

HWVP Feed (with noble metals precipitated w/ minor constituents)

In the colder end of the sample (below 700°C), noble metals were clearly identifiable as particles separate from the other waste components. Some of the particles were found amidst other

wastes, but many were located at the interface between the waste and the frit particles. Individual particles in this region were generally <5 μm in size, and were either pure RuO_2 or a mixture of Ru and Pd. An example of typical sliver-shaped RuO_2 crystals present at 619°C is shown in Figure 1. Some large agglomerates of up to 40 μm were present in this temperature region (see Figure 2). These results at relatively low temperatures (below 700°C) indicate that distinct noble metal particles and agglomerates can exist in dried feed and therefore in the cold cap of a melter.

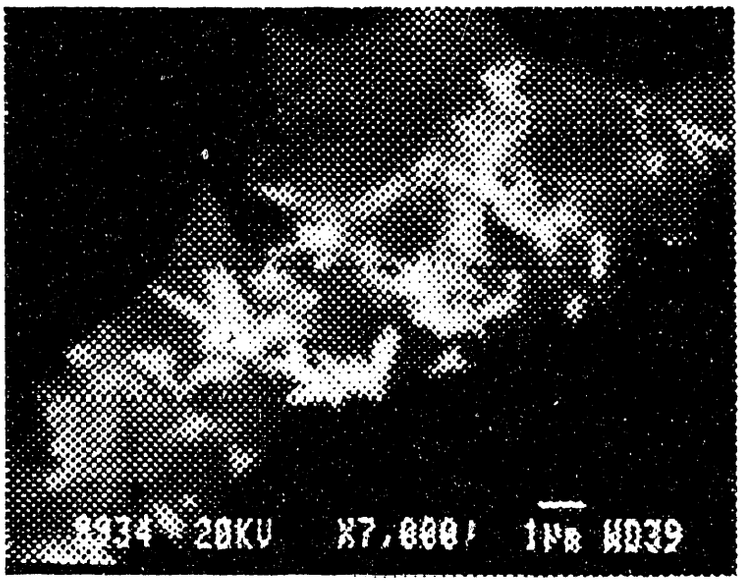

Figure 1. Cluster of RuO_2 Crystals in HWVP Sample at 619°C

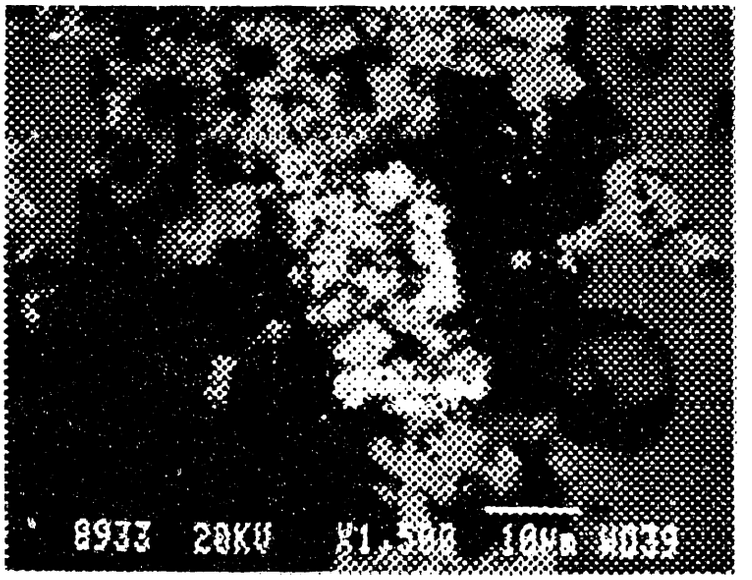

Figure 2. Large Pd/Ru Mass in HWVP Sample at 600°C

No major changes in noble metal particle characteristics were seen between the lower temperature region and regions up to 800°C. The melt as a whole experiences a great deal of change at

these temperatures, as large amounts of waste begin to dissolve and become an integral part of the glass matrix[7]. However, the noble metal particles seem largely unchanged.

At temperatures beyond 800°C, more large clusters were present; however, small particles were still very common. Rhodium was detected as a 10-μm cluster of solid, dense particles. Pd was generally seen only in particles mixed with Ru, not in a pure state. At the hottest temperature region (approximately 880°C - 936°C), most particles were small (<5 μm) and almost all were RuO_2. No Pd particles were found in this region. This suggests that the small amount of Pd present in the waste is soluble at these temperatures.

To provide input to the computer modeling effort, two sections at the hottest end (approximately 930°C) of this HWVP sample were examined in detail. The number, size, shape, and approximate composition of the particles or agglomerations were determined. The particles at this temperature are assumed to be representative of particles leaving the cold cap and entering the bulk of the melt. This is considered to be a boundary condition for the computer model.

All noble metal particles in the sections examined were classified by particle size and shape and then divided into categories. Average characteristics for each group were determined. An "effective particle diameter" for each group was determined by using the total particle area and assuming a spherical shape. This parameter was used in initial computer modeling. A summary of the particle characteristics is shown in Table 2. The density and electrical conductivity of the particles can be assumed to be equal to that of RuO_2, because over 99% of the particles seen were ruthenium dioxide.

Table 2. Particle Characteristics of HWVP Feed (with minors) at 930°C

Characteristic	Group 1	Group 2	Group 3
Shape	solid sphere	agglomerate	agglomerate
Predominant type	RuO_2	RuO_2	RuO_2
Effective Particle Diameter(a)	1.3 microns	3.8 microns	12.4 microns
Particles/Melt Area (number/mm^2)	34	16.3	0.33

(a) The diameter is calculated using total particle area and assuming a spherical shape of the particle or agglomerate.

HWVP Feed (with noble metals precipitated w/ major constituents)

The HWVP (with majors) sample was similar to the HWVP (with minors) sample in that dried feed at the colder end of the crucible contained agglomerates of noble metals, particularly Ru and Pd. An example of such an agglomerate is shown in Figure 3 at 592°C. However, differences were apparent between the two feeds. Particles at the hot end of the HWVP (with majors) sample were larger overall than in the HWVP (with minors) sample,

varying in size between 1 μm and 10 μm. Another difference was the presence of Pd at temperatures above approximately 900°C in this feed.

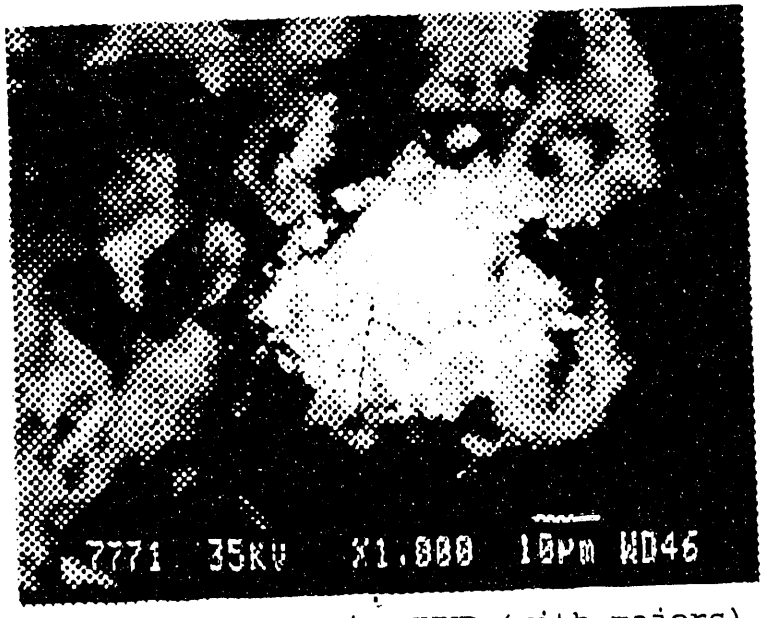

Figure 3. Pd in Cd-rich Area in HWVP (with majors) Sample at 592°C

DWPF Feed

The most significant difference between this feed and the HWVP (with minors) feed is that no identifiable noble metal particles were present below 735°C. The lack of detectable particles suggests that they exist as sub-micron particles in the high-Fe waste particles, undetectable by SEM/EDS.

Between 735°C and 840°C, Pd, Rh, and Ru were all identified as fairly dense particles of 2 μm or smaller size (see Figure 4). Above 840°C, some larger particles existed, up to approximately 10 μm. These particles did not resemble the sliver- or needle-shaped RuO_2 particles in the HWVP (with minors) sample. They instead resembled solid or porous chunks.

KfK Feed

Both the number and size of noble metal particles and agglomerates were much larger in the KfK feed than in the other feeds, due to the higher concentrations present in the feed. As in the HWVP feeds, large agglomerates of RuO_2 were present at relatively low temperatures. For example, Figure 5 shows a large (1-mm) RuO_2 chunk at 704°C. A few irregularly-shaped 5- to 10-μm RuO_2 or Pd particles were also seen in this region. At temperatures below approximately 850°C the noble metals are also commonly mixed with other elements, such as Fe, Zr, and Ni, that are present in the waste.

Between 874°C and 1039°C, Ru and Pd became common as large (up to 15 μm) diffuse Ru patches surrounded by dense, submicron Pd particles. Large (100-μm and 500-μm) masses of crystalline RuO_2

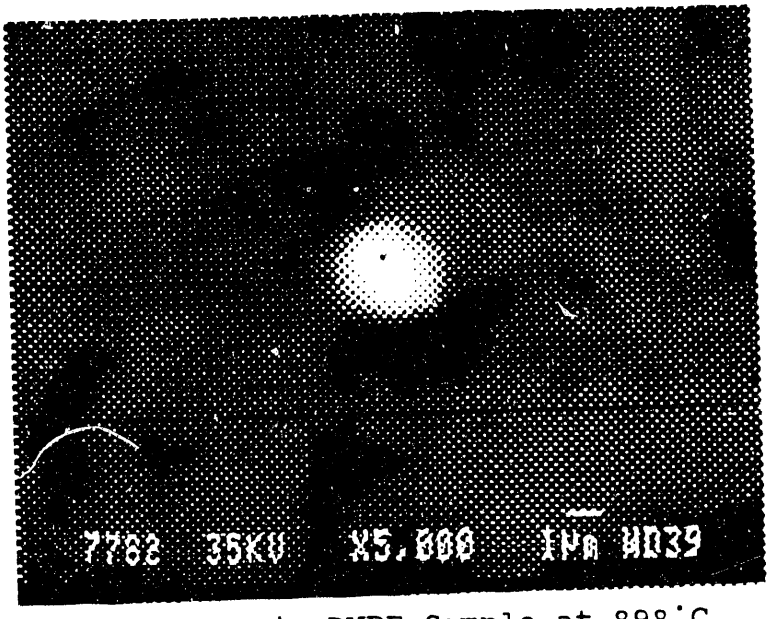

Figure 4. Ru/Rh/Pd Alloy in DWPF Sample at 898°C

particles were seen at approximately 878°C. These masses consisted of small, mostly sliver-shaped crystals, with a few larger crystals present (see Figure 6).

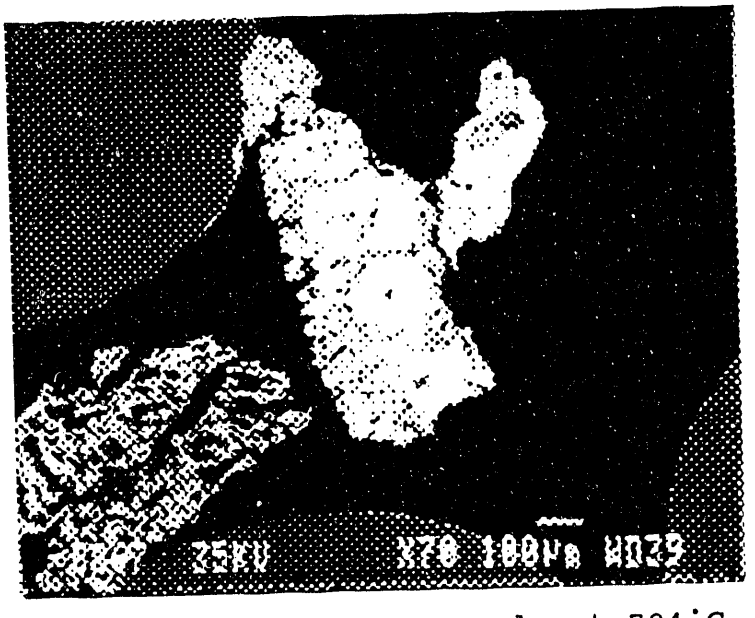

Figure 5. Large RuO_2 Chunk in KfK Sample at 704°C

CONCLUSION

The following conclusions can be made based on the results of the gradient furnace tests:

- Noble metals became concentrated in dried feed in HWVP and KfK feeds, suggesting that agglomeration of noble metals occurs during simulant preparation and drying. These agglomerates were as large as 40 μm in the HWVP (with minors) sample and as large as 1 mm in the KfK sample at temperatures below approximately 700°C. The dried,

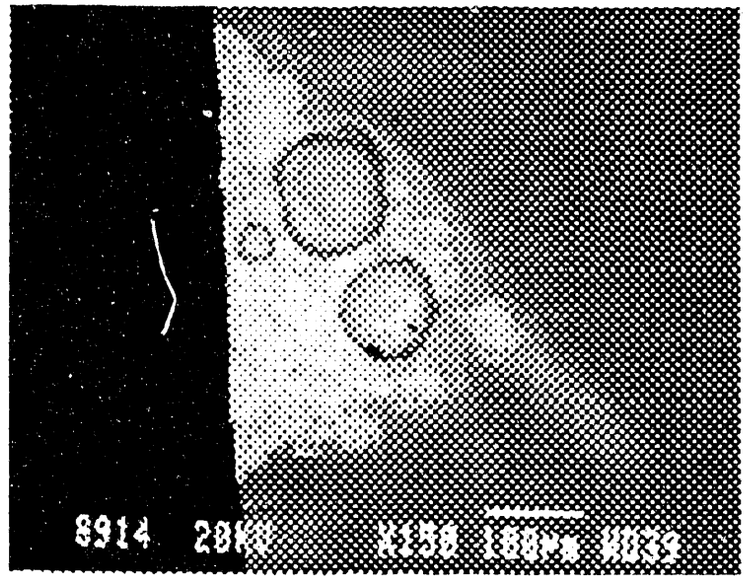

Figure 6. Large Mass of RuO_2 Crystals in KfK Sample at 878°C

unreacted, DWPF feed did not contain any such agglomerates.

- In all feeds, noble metals had separated from other waste constituents and formed pure metal, metal oxide, or alloyed particles by approximately 800°C.
- At the highest temperatures studied (928°C - 1046°C, depending on the feed), noble metal particle or clusters of particles were generally less than 10 μm for all feeds studied. However, agglomerations of RuO_2 particles up to 500 μm were seen in the KfK sample.

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